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AUGER ELECTRON SPECTROSCOPY STUDIES OF OXIDE FILMS ON AL-ZN-MG --ETC(U)
JUL 79 R K VISWANADHAM, T S SUN, J A GREEN N00014-74-C-0277
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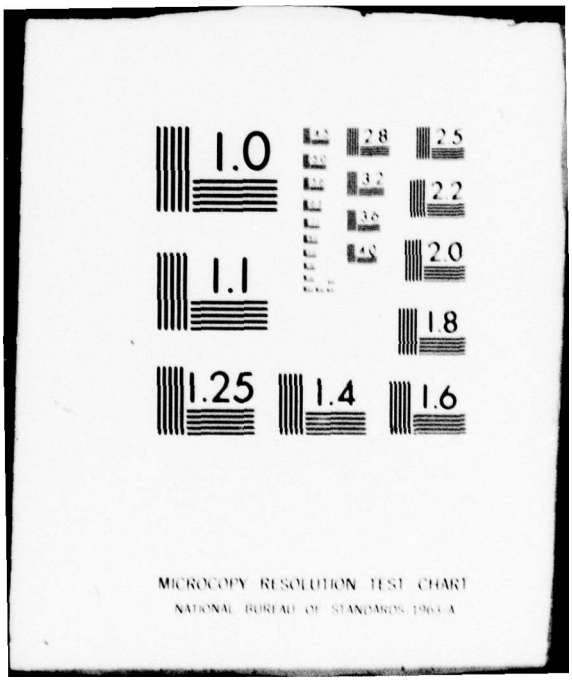
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AUGER ELECTRON SPECTROSCOPY STUDIES OF OXIDE FILMS ON Al-Zn-Mg ALLOYS

Prepared by:

R.K. Viswanadham, T.S. Sun and
J.A.S. Green

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(6) Auger Electron Spectroscopy Studies of Oxide Films on Al-Zn-Mg Alloys,

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Abstract

Auger electron spectroscopy and depth profiling have been used to obtain information on the composition of oxide films formed on high purity Al-5.5Zn-2.5Mg alloys as a function of heat treatment, grain size, storage environment and temperature. These studies show that in the as-heat-treated condition the oxide film is predominantly MgO. The Mg/O peak-to-peak height ratio of this oxide is sensitive to the heat treatment temperature and exhibits a maximum at 475°C. During subsequent storage, especially in a moist environment, this film undergoes substantial changes in composition. The Mg/Al ratio of the oxide decreases due to formation of an Al-rich oxide on top of the as-heat-treated oxide. A model is proposed to account for the changes in the oxide film composition during growth of the Al-rich oxide, and possible implications to pre-exposure embrittlement and stress corrosion cracking are discussed.

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I. INTRODUCTION

Stress corrosion cracking (SCC) in Al-Zn-Mg alloys has been the subject of numerous investigations. Recent evidence seems to indicate that hydrogen embrittlement and anodic dissolution both play a role in stress corrosion cracking of these alloys,[1-3] and of these, hydrogen embrittlement appears to be the dominant mechanism.[3] Accepting this, it is then essential to consider the following steps:

1) Generation of hydrogen
2) Entry of hydrogen through the surface film, and
3) Concentration of hydrogen in a localized region to cause embrittlement.

Each of these steps is governed by a complex interplay between the alloy and the environment. Since SCC in these alloys is intergranular, it follows that segregation of alloying elements to the grain boundary is an important factor in determining the resistance of these alloys to cracking. Auger electron spectroscopy (AES) studies in these alloys have shown that Mg and Zn segregate to grain boundaries during the quench from the solution temperature and this segregation is subsequently modified by precipitation.[4,5]

However, segregation not only influences the local electrochemistry of the grain boundary region, but can also modify the nature of the overlying oxide. Since pure aluminum oxide is an effective barrier against hydrogen dissociation and entry,[6] it is possible that incorporation of grain boundary segregates into the film may reduce its protective nature. Consequently, efforts were made using AES to determine the composition of the oxide films formed on Al-Zn-Mg alloys as a function of solution treatment temperature and grain size, and to examine the influence of subsequent storage in moist and dry environments.

II. EXPERIMENTAL RESULTS

A. Composition of As-Heat-Treated Oxide Films

The studies of oxide film composition were conducted on a high purity Al-5.5 wt% Zn-2.5 wt% Mg alloy. Strips of the alloy were heat-treated at 475°C for 10 minutes and for 2 hours in flowing, dry argon -- yielding grain sizes of 0.08 and 0.25 mm, respectively. The samples were then water-quenched and cleaned, dried, and transferred to the spectrometer for AES and depth profiling measurements. AES measurements show that for both grain sizes, the oxide films are considerably enriched in Mg. Other investigators have observed similar results.[7,8] The depth profiles of oxide films on the two samples are shown in Fig. 1. For the large grain size samples, the oxide film is thicker due to the longer heat-treating time. Except for this difference, the oxide film on both samples is essentially MgO, with little Al and virtually no Zn content.

To evaluate the influence of temperature on the composition of the oxide film, samples were heat-treated at 450°, 465°, 475°, and 500°C, and the composition of the oxide film was analyzed by AES. The results (Fig. 2) show that the Mg content of the oxide exhibits a maximum at ~ 475°C. The reason for this maximum is probably the competition between two reactions, namely the reaction between Mg and O_2 and the evaporative loss of Mg. While Mg has significant vapor pressure at most temperatures of solution treatment, it appears that below ~ 475°C the reaction between Mg and O_2 dominates and the concentration of Mg in the film increases. On the other hand, at temperatures above ~ 475°C evaporative losses of Mg are predominant and result in lower concentrations of Mg in the oxide. This view is also consistent with variations in the thickness of the oxide, which decreases at temperatures above ~ 475°C.

B. The Influence of Storage on the Composition of Oxide Films

Substantial changes in the chemistry of the films take place upon storage. The Mg content of the oxide films decreases upon storage in both dry and moist (100% RH) environments at 50°C (Fig. 3). In the case of both the small and large grain size samples, the decrease of the Mg content of the film appears to be more rapid under moist conditions, possibly suggesting Mg dissolution into adsorbed layers of moisture. The depth profile of the oxide film on a small grain sample after storage in a moist environment at 50°C is shown in Fig. 4. Here, it may be seen that Mg is still present at the metal-oxide interface, indicating that oxidation during storage has resulted in the formation of an Al-rich oxide on top of the as-heat-treated film -- the Mg serving to locate the original metal-oxide interface.

In addition to the overall decrease in the Mg content of the oxide, illustrated in Fig. 3, the films formed upon storage of the large grain samples show substantial local variations in composition. These compositional variations are evidenced by a patchy appearance of the film -- the oxide was visibly dark and white. The AES depth profiles for the two types of areas are shown in Fig. 5. The dark areas are found to be rich in Mg, while the white areas are Al-rich. The depth profile of the Mg-rich areas on the oxide film is very similar to that of the initial as-heat-treated film; whereas, the oxide film in the Al-rich areas is substantially thicker and quite distinct from the as-heat-treated film. Note that while these compositional variations were most evident on the large grain samples, similar variations can presumably occur in finer grain material, though will be less obvious.

We believe these compositional changes can be explained by a model such as that represented schematically in Fig. 6. During heat treatment it is assumed that the Mg-rich oxide nucleates at the grain boundaries of the substrate (Fig. 6a). This assumption is valid for two reasons:

1) No substantial decrease in the Mg content of the substrate beneath the as-heat-treated film is observed in the AES studies.
2) The grain boundaries can serve as short-circuit diffusion paths for Mg segregated there. The Mg atoms can then diffuse along the boundaries to reach the surface.

Upon growth, these areas would soon impinge and the surface would be covered with a MgO layer, (Fig. 6b), as has been observed. The areas of impingement would form internal boundaries in the as-heat treated film, the location of which may or may not have any spatial relationship to the grain boundaries in the substrate. During subsequent storage of the samples in various environments, Al ions may preferentially diffuse along these boundaries in the oxide, and Al-rich oxide layers would subsequently nucleate and grow superficially from these boundaries (Fig. 6c). Hence, if an AES depth profile were to be taken at this stage, one would observe two types of areas: 1) thin Mg-rich oxide areas (Fig. 5a), and 2) thicker, mixed Al-Mg oxide areas, Fig. 5b. This is exactly what is observed. Of course, the distinction between the two types of areas is not as clear-cut as is schematically illustrated in Fig. 6, presumably due to some inter-diffusion of Mg and Al.

C. Effect of Oxide Film Composition on Pre-Exposure Embrittlement and Stress Corrosion Cracking

A study of pre-exposure to moist environments and subsequent embrittlement of high purity Al-Zn-Mg alloys has been actively pursued by Swann and his co-workers.[9,10] In these studies, hydrogen was detected during fracture of pre-exposed samples and has been identified as the embrittling species. Further, the severity of pre-exposure embrittlement was found to be sensitive to solution treatment temperature as was the type of oxide film present on the surface of the sample. As-heat-treated oxide films were found to enhance the degree of pre-exposure embrittlement.[9]

Some results obtained by Scamans, Alani, and Swann on the pre-exposure embrittlement of Al-Zn-Mg alloys of roughly similar composition to those of the present study are reproduced in Fig. 2b.[9] The degree of embrittlement is plotted as a function of the solution treatment temperature. As seen, the temperature at which the Mg content of the oxide is a maximum is also the temperature at which there is minimum ductility, or maximum pre-exposure embrittlement. This result suggests a correlation between the Mg content of the film and susceptibility to pre-exposure embrittlement.

III. DISCUSSION

AES studies of the composition of oxide films formed on Al-Zn-Mg alloys clearly show that the as-heat-treated film is essentially MgO. Further, it appears that this film undergoes substantial changes in thickness and composition due to overgrowth of partially hydrated oxides of aluminum. The reaction between the outward diffusing Al^{3+} ions and H_2O present in the exposure environment will lead to the formation of hydrogen ions

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$$

In a previous report,[11] the formation of Mg-H complexes was proposed as a means of enhancing the concentration of hydrogen at grain boundaries. In an analogous manner Mg present in the film presumably can also strongly bind with hydrogen, the recombination of atomic hydrogen to molecular hydrogen is thus minimized, and hydrogen has more time to diffuse into the grain boundaries. In the absence of Mg or Mg-rich films, the atomic hydrogen probably will simply recombine and escape as molecular hydrogen. This is the most likely explanation for the observed correlation between pre-exposure embrittlement and the Mg content of the oxide.

IV. SUMMARY

1) AES studies show that the as-heat-treated oxide films on Al-Zn-Mg alloys are essentially MgO. The thickness and the Mg content of these films is sensitive to the heat treatment temperature and time.

2) During storage, the as-heat-treated oxide undergoes significant changes in chemical composition. The principal change is the formation of an Al-rich oxide on top of the Mg-rich oxide.

3) A model is proposed to account for the observed changes in chemical composition of the as-heat-treated oxide films during storage.

4) During formation of the Al-rich oxide, the reaction of Al^{3+} ions with H_2O vapor in the environment has been shown by other workers[9,10] to lead to pre-exposure embrittlement. From these studies, it appears that the extent of pre-exposure embrittlement is sensitive to the Mg content of the as-heat-treated oxide.

Acknowledgement

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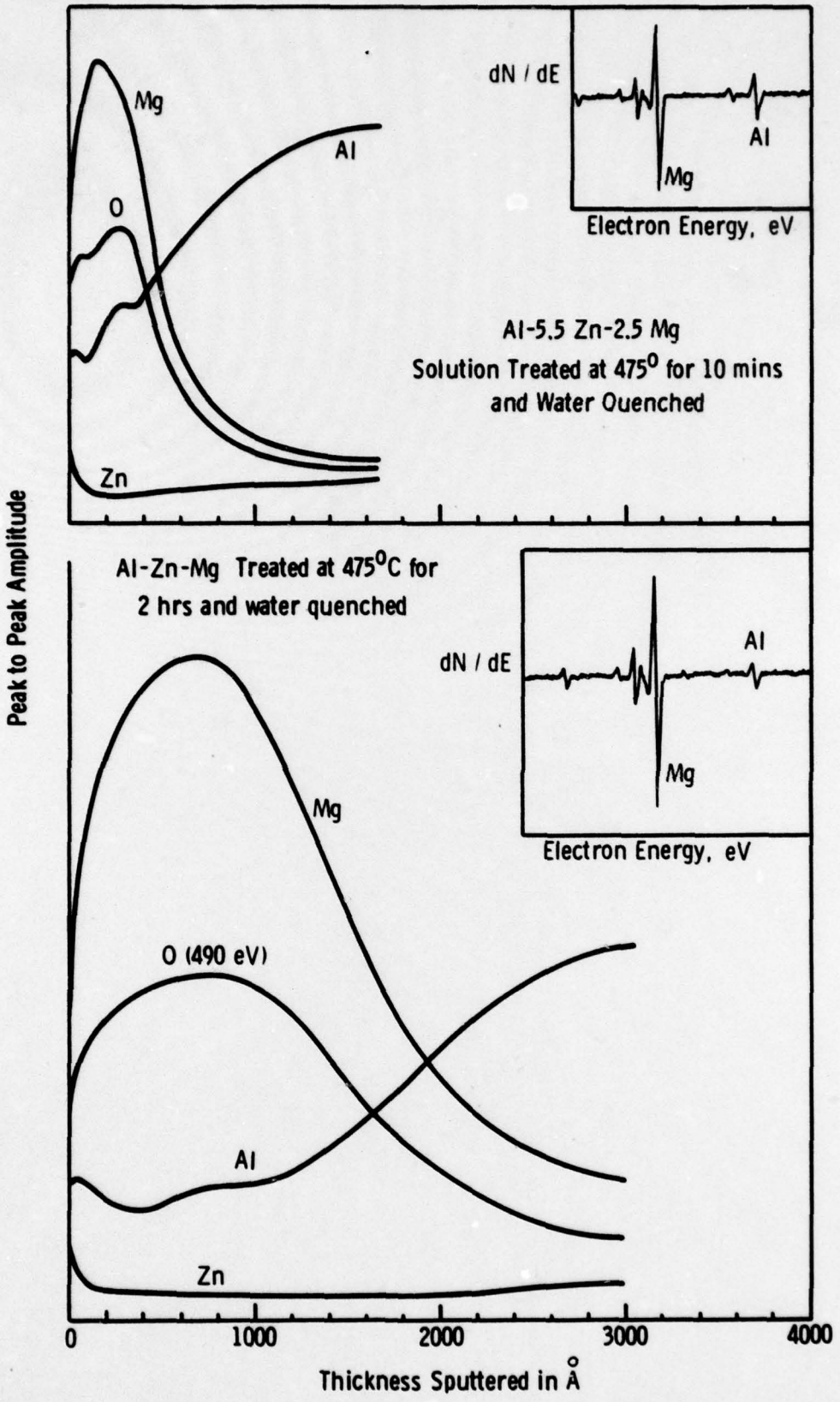

Figure 1. Auger depth profiles of the as-heat treated oxide films on Al-Zn-Mg alloys of different grain sizes.

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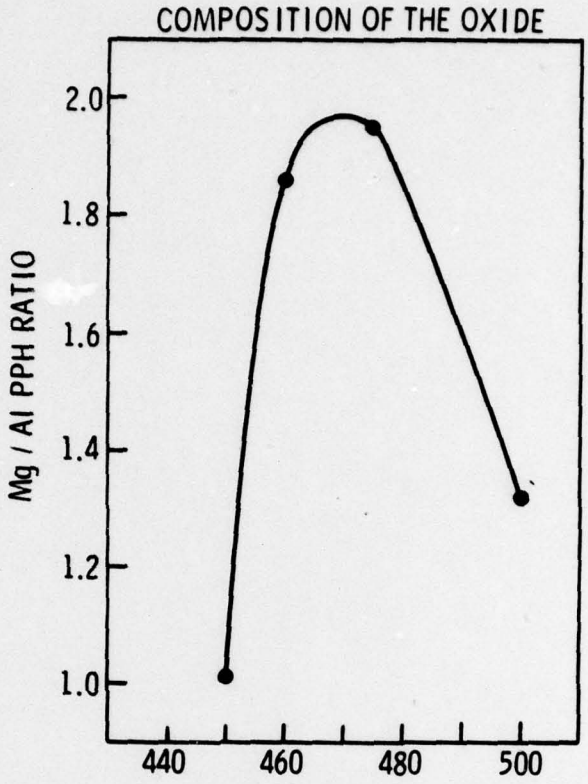

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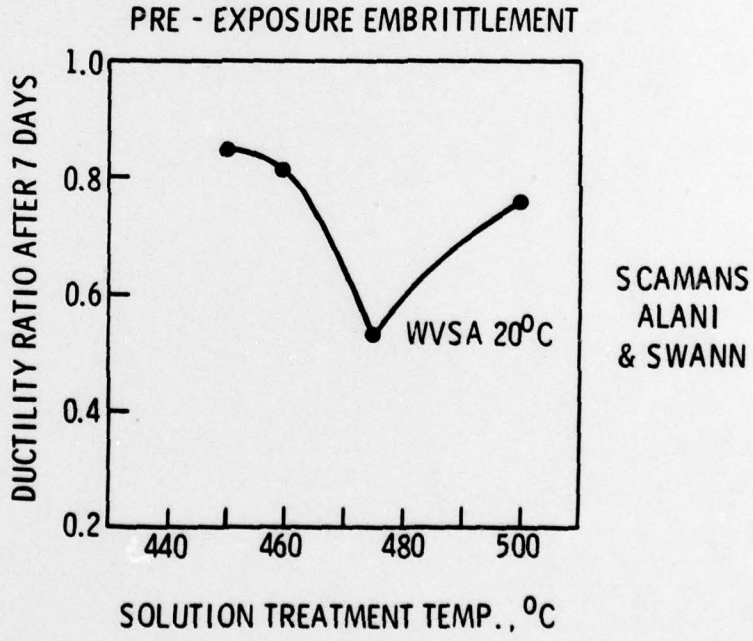
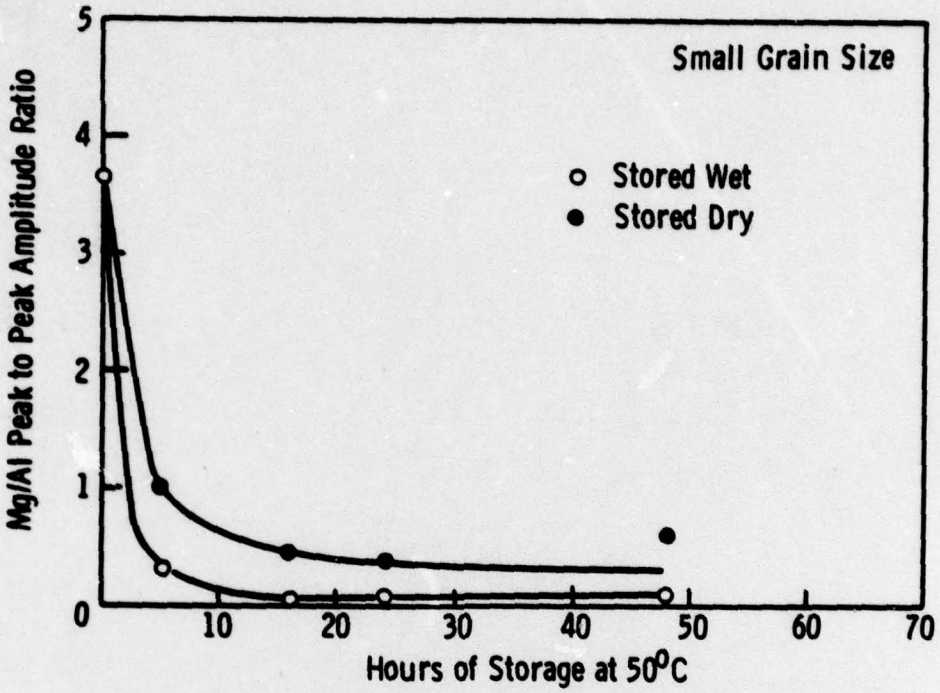


Figure 2. Changes in the Mg content of the as-heat-treated oxide film on Al-Zn-Mg alloys as a function of solution treatment temperature, Fig. 2a, and its correlation to the degree of pre-exposure embrittlement, Fig. 2b, after the work of Scamans, Alani, and Swann.(9)



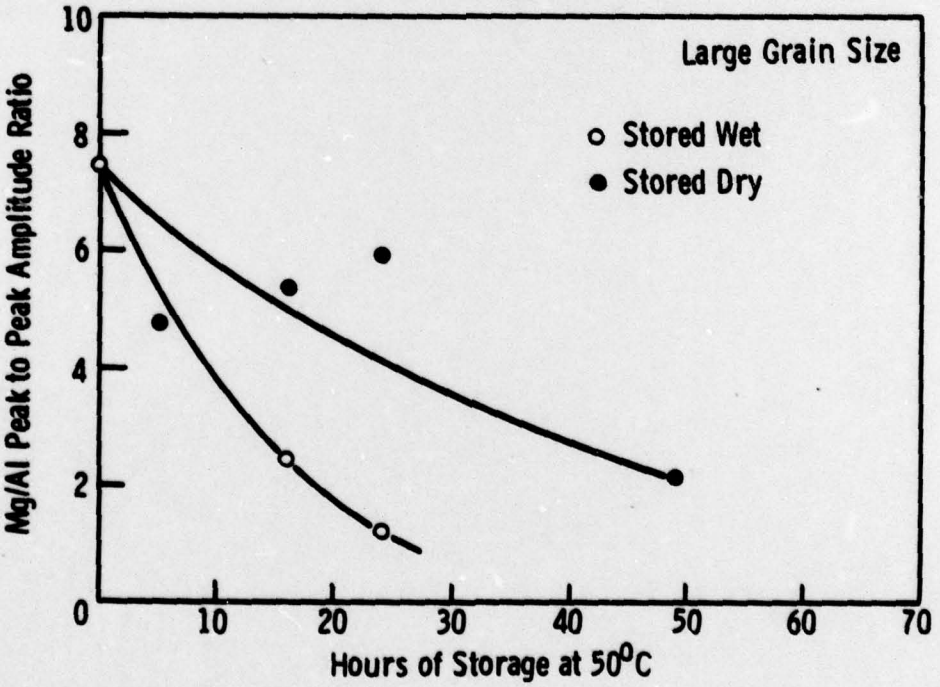


Figure 3. Changes in the chemical composition of the as-heat-treated oxide films formed on Al-Zn-Mg alloys during storage in wet and dry environments at 50°C.

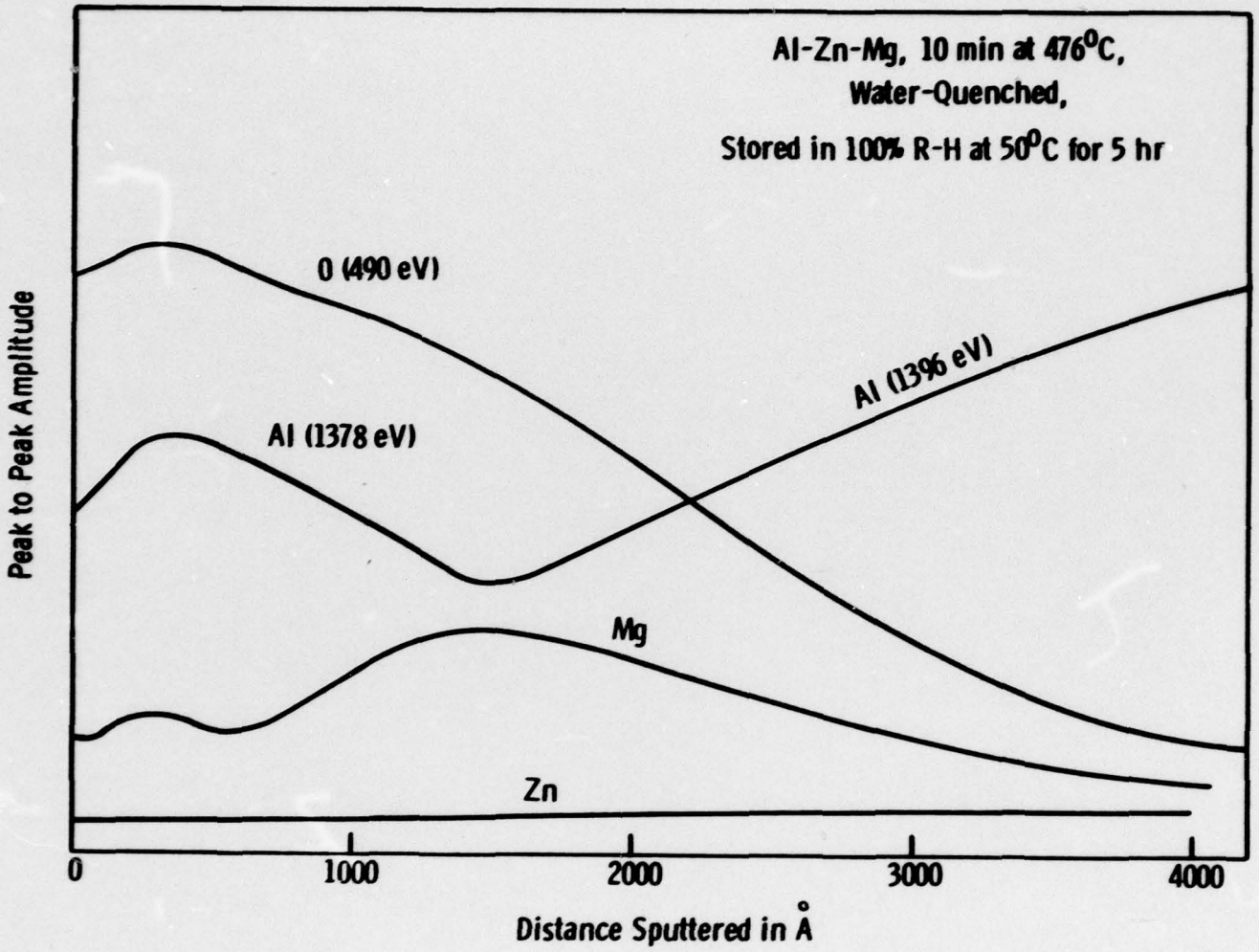


Figure 4. Auger depth profile of the oxide film on a small grain Al-Zn-Mg alloy after storage in a wet environment at 50°C.

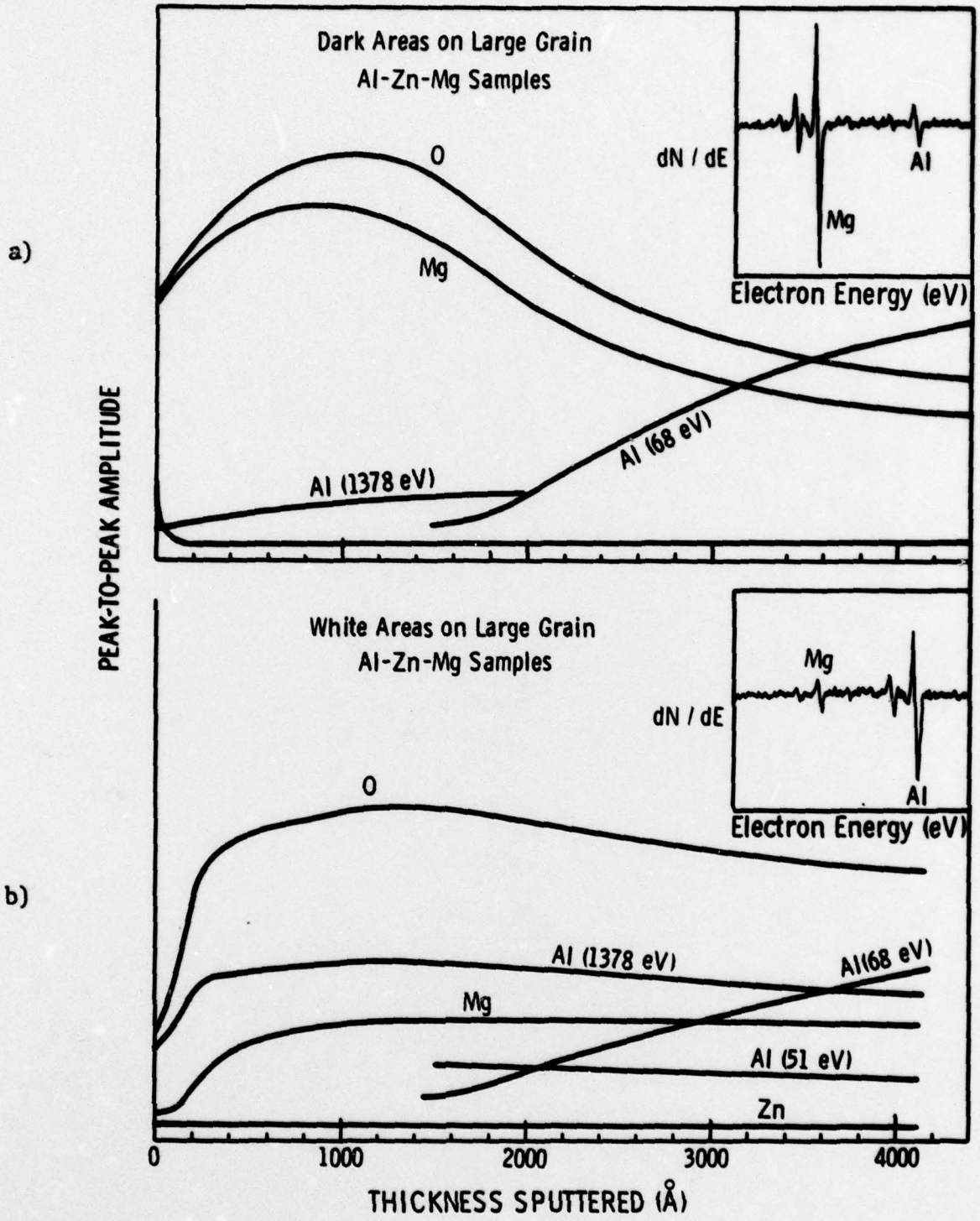


Figure 5. Auger depth profiles of the Mg-rich (dark) and Al-rich (white) areas that develop on large grain Al-Zn-Mg alloys upon storage in a wet environment at 50°C.

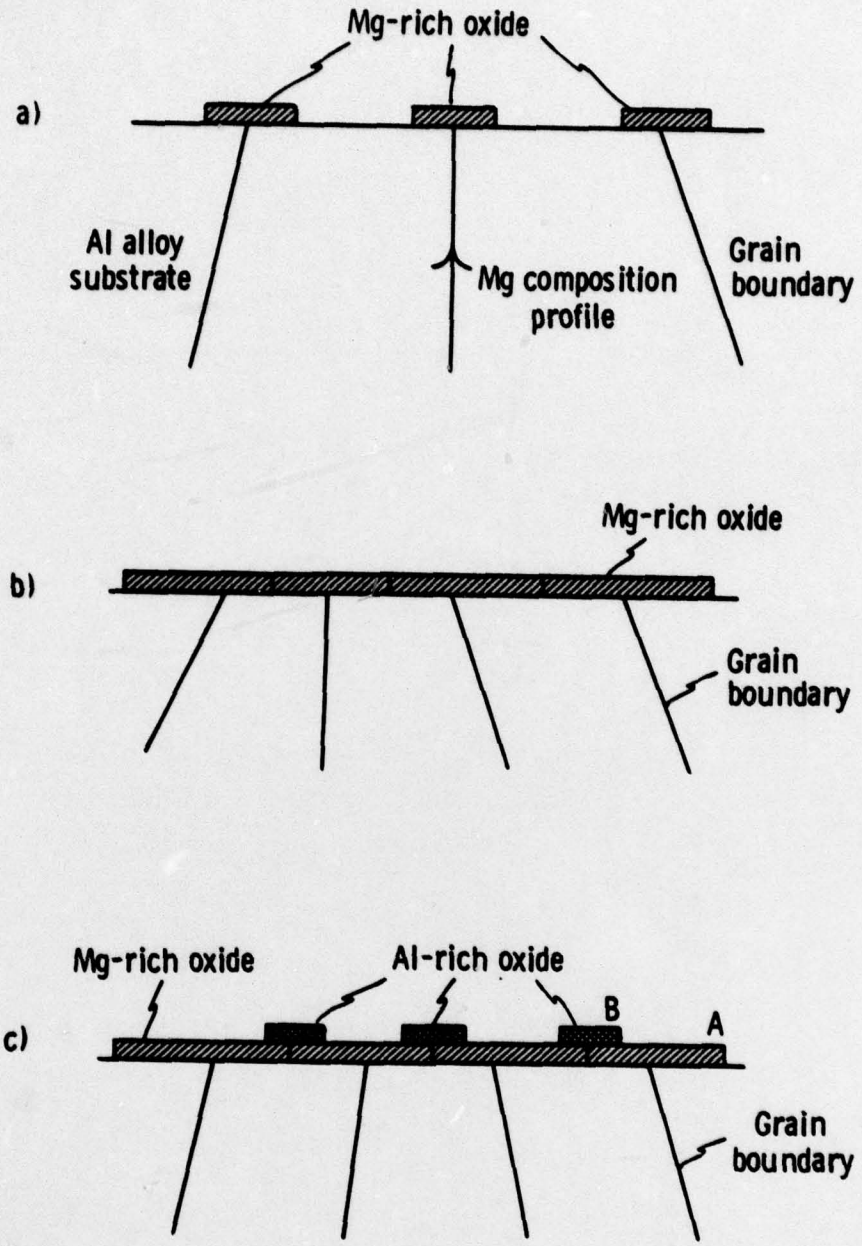


Figure 6. A schematic representation of the formation of the as-heat-treated oxide film and the chemical changes that ensue upon storage on large grain Al-Zn-Mg alloy samples.